

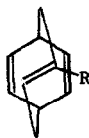
PHOTOCHEMICAL ADDITIONS OF 1,3-DIENES TO BENZENE

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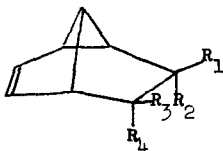
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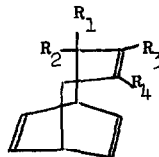
Photochemical additions of benzene to alkenes have been a subject of current interest,^{1,2,3} but only preliminary investigations have been reported on the corresponding reactions with 1,3-dienes.⁴ Kraft and Koltzenberg found that benzene reacted photochemically with 1,3-butadiene and isoprene to give complex mixtures of products even at very low conversions. Major portions of the isolable products may be derived from two primary photochemical processes, a $4\pi_s+4\pi_s$ photocycloaddition to give a 3-trans isomer of bicyclo[4.2.2]deca-3,7,9-triene (1), and 1,2-addition of the diene to the 1,3-positions of benzene to give tricyclo[3.3.0.0^{2,8}]oct-3-enes (2). Compound 1a (R=H) or 1b (R=CH₃) either dimerized to give a 2:2 adduct or reacted with the diene to give 1:2 adducts and thus could not be isolated. On the other hand, benzene reacted with 2,3-dimethyl-1,3-butadiene to give mainly 1:1 adducts which were not characterized. The difference between the behaviors of these dienes was not understood.⁴ We have found that the $4\pi_s+4\pi_s$ photocycloaddition of 2,4-dimethyl-1,3-pentadiene (DMPD) and 2,3-dimethyl-1,3-butadiene (DMBD) to naphthalene and to anthracene gave the benzo and the dibenzo derivatives of 3-cis-bicyclo[4.2.2]deca-3,7,9-triene (3) while other acyclic dienes gave the benzo and the dibenzo derivatives of the 3-trans isomer (1). These observations indicate that the ground state conformation of 1,3-dienes will determine the structure of the adduct and the s-cisoid conformation of 1,3-dienes may be more reactive than the corresponding s-transoid conformation.^{5,6} This communication deals with the photocycloaddition of benzene to the s-cisoid DMPD parallel to that of benzene to DMBD which may lead to a better understanding on the photochemical behaviors of benzene.



1



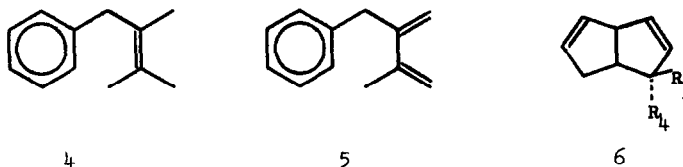
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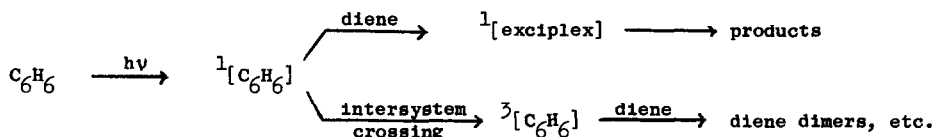
Irradiation of a solution of DMED (0.24 mole) in benzene (1.2 moles) with a Hanovia 450-W lamp for 21-144 hr yielded a complex mixture of products. The quartz cooling well became coated with polymeric material after a few hours and was cleaned after every 24 hr of irradiation. Approximately 2.4 g of products were formed per 24 hr of irradiation, and the nature of products did not vary appreciably during the irradiation. Mass spectral analysis of the vpc fractions of the irradiation mixture revealed the presence of at least 3 dimers of the diene, 7 1:1 adducts and higher molecular weight material. None of the product was formed in higher than 10% yield. The mixture was separated by distillation at 2 mm followed by extraction with 20% aq. AgNO_3 and preparative vpc at 140° (on a $3/8'' \times 15'$ 20% Carbowax 20M on Chromosorb P column). Three major (3a, 2a and 2b) and two minor (4 and 5) adducts were isolated in pure form and a fourth major adduct was isolated in impure form.⁷ Compound 3a was isolated from the AgNO_3 extracts while the other products were isolated by preparative vpc of the distillate after it had been extracted with AgNO_3 .

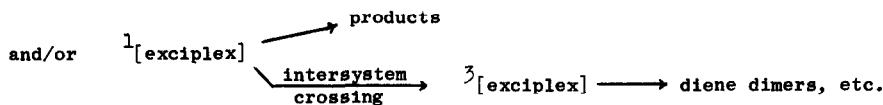
Compound 3a ($R_1=R_2=H$, $R_3=R_4=CH_3$) is the $4\pi_g+4\pi_g$ adduct which exhibits: bp $115-120^\circ$ (20 mm); ir (neat) 1640 cm^{-1} ; uv end absorption; nmr (CCl_4) δ 1.52 (s, 6, CH_3), 2.50 (m, 4, CH_2), 2.90 (m, 2, CH) and 5.93 ppm (m, 4, $\text{CH}=\text{CH}$). Compound 2a and 2b exhibit the characteristic spectral properties of the tricyclo[3.3.0.0^{2,8}]oct-3-enes.³ Compound 2a ($R_1=R_2=H$, $R_3=C(\text{CH}_3)=\text{CH}_2$, $R_4=CH_3$) exhibits: nmr (CCl_4) δ 1.20 (s, 3, CH_3), 1.68 (m, 3, $\text{C}=\text{C}-\text{CH}_3$), 1.25-1.95 (m, 4, CH), 2.40 (q, 1, $J = 5.5\text{ Hz}$, C^1H), 2.80 (2t, 1, $J = 2$ and 5.5 Hz , C^5H), 4.56 (m, 2, $\text{C}=\text{CH}_2$), 5.28 (2d, 1, $J = 2$ and 5.5 Hz , $\text{CH}=\text{CH}$) and 5.52 ppm (2d, 1, $J = 2$ and 5.5 Hz , $\text{CH}=\text{CH}$). Compound 2b ($R_1=R_2=H$, $R_4=C(\text{CH}_3)=\text{CH}_2$, $R_3=CH_3$) exhibits: nmr (CCl_4) δ 0.92 (s, 3, CH_3), 1.75 (m, 3, $\text{C}=\text{C}-\text{CH}_3$), 1.00-2.12 (m, 4, CH), 2.35 (q, 1, $J = 5.5\text{ Hz}$, C^1H), 2.93 (2t, 1, $J = 2$ and 5.5 Hz , C^5H), 4.52-4.90 (m, 2, $\text{C}=\text{CH}_2$), 5.50 (2d, 1, $J = 2$ and 5.5 Hz , $\text{CH}=\text{CH}$) and 5.68 ppm (2d, 1, $J = 2$ and 5.5 Hz , $\text{CH}=\text{CH}$). The stereochemical assignments of the 6-methyl and the 6-isopropenyl groups in 2a and 2b were based on their nmr spectra that the chemical shift of the exo methyl group occurs at the higher field.^{2,3} When 2a or 2b was heated for 30 min at 250° in a sealed tube, it underwent a smooth 1,5-sigmatropic shift of the 7-H to give bicyclo[3.3.0]octa-2,5-dienes 6a or 6b respectively in quantitative yield. Such a shift which has been reported previously by Srinivasan in analogous systems establishes the positions of the two alkyl substituents in 2a and 2b to be at the C-6.² The spectroscopic properties of the impure fourth major adduct suggest that it is a tricyclo[3.3.0.0^{2,8}]oct-3-ene and probably 2c ($R_3=R_4=H$, $R_1=CH_3$, $R_2=C(\text{CH}_3)=\text{CH}_2$). The structures of the two minor products were identified by their spectroscopic properties to be 4 and 5.



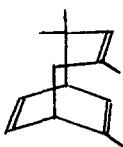
Irradiation of a solution of DMPD (0.24 mole) in benzene (1.2 moles) under similar conditions for 96 hr yielded a clear solution with no visible deposit on the cooling well. The solution was evaporated, dissolved in pentane and extracted with 20% aq. AgNO_3 . Compound 3b ($R_1=R_2=R_4=\text{CH}_3$, $R_3=\text{H}$) (2.1 g, 37%) which was isolated from the extract exhibits spectroscopic properties compatible with the assigned structure: bp $60.5\text{--}62.0^\circ$ (2 mm); mass spectrum, parent peak (m/e) 174; uv end absorption; ir (neat) 1675 , 1635 and 780 cm^{-1} ; nmr (CCl_4) δ 1.05 (s, 6, CH_3), 1.60 (s, 3, $\text{C}=\text{C}-\text{CH}_3$), 2.26–2.68 (m, 3, CH_2 and C^1H), 2.83 (m, 1, C^6H), 4.56 (m, 1, C^3H) and 6.00 ppm (m, 4, $\text{CH}=\text{CH}$). In addition to non-volatile material (2.4 g, 42%), a complex mixture of 1,3-adducts (1.2 g, 21%) but no dimers of DMPD were isolated from the pentane solution after the extraction. So far we have not been able to resolve the mixture into individual components. The reaction provides a rapid and convenient synthesis for the bicyclo[4.2.2]deca-3,7,9-triene system.

In contrast to DMBD, DMPD has been shown to be an effective quencher of photoexcited naphthalene,^{5,8} and an exciplex between the excited aromatic compound and the diene has been suggested as the intermediate in the quenching.^{6,8} Our results on the photocycloaddition of benzene to 1,3-dienes are in agreement with these findings. Photoexcited benzene will react with DMPD to give 3b as the major product, while it will react with DMBD to give a variety of products including the dimers of the diene which may be derived from the triplet state of benzene. On the basis of our observations, we wish to propose that photoexcited benzene may undergo two competitive processes in the presence of a 1,3-diene, the photochemical reactions and the intersystem crossing. The relative importance of these two processes will depend on the reactivity of the diene used. The intersystem crossing may occur from the isolated photoexcited benzene or the exciplex.





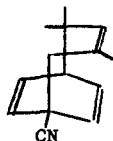
Preliminary investigation on the photochemical addition of DMPD to toluene and to benzonitrile indicated that toluene gave 7a and 7b as the major adducts while benzonitrile gave 7c and 7d as the major adducts, i. e., an electron donating substituent in benzene directs the addition of the diene mainly to the unsubstituted positions while an electron withdrawing substituent directs the addition mainly to the substituted position. The results suggest that the diene probably acts as the electron donor component and the photoexcited aromatic compound acts as the electron acceptor component in the photocycloaddition. This investigation is being continued.



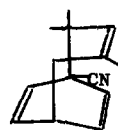
7a



7b



7c



7d

Acknowledgement. The authors wish to thank the National Institutes of Health, Grant AM-11676, and the National Science Foundation for the support of this work.

Footnotes

- (1) K. E. Wilzbach and L. Kaplan, J. Amer. Chem. Soc., **93**, 2073 (1971) and earlier work.
- (2) R. Srinivasan, Tetrahedron Letters, 4551 (1971) and earlier work.
- (3) A. Morikawa, S. Brownstein, and R. J. Cvetanovic, J. Amer. Chem. Soc., **92**, 1471 (1970).
- (4) K. Kraft and G. Koltzenberg, Abst. Internat. Conf. Photochem. (Munich), 439 (1967) [Chem. Abst., **70**, 57309g (1969)]; Tetrahedron Letters, 4357 and 4723 (1967).
- (5) N. C. Yang, J. Libman, et al., J. Amer. Chem. Soc., **95**, 1405, 1406, 9226 and 9228 (1972).
- (6) D. A. Labianca, G. N. Taylor, and G. S. Hammond, ibid., 3679; G. N. Taylor and G. S. Hammond, ibid., 3684 and 3687.
- (7) All new products gave correct elemental analyses and spectral properties compatible to the assigned structures, but only the spectral data not previously reported and essential for our discussion are reported.
- (8) L. M. Stephenson and G. S. Hammond, Pure Appl. Chem., **16**, 115 (1968).